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(54) Ziegler-Natta catalysts with metallocenes for olefin polymerization

(57) This invention relates to a process for making a catalyst in which a metallocene is included in the synthesis of a Ziegler-Natta catalyst and a process for using the catalyst in the polymerization of olefins, specifically, propylene, to produce a polymer product with broad polydisperisty.

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Description

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION: This invention relates to catalyst system for the polymerization of olefins, particularly, to a catalyst system comprising a supported Ziegler-Natta catalyst which has been modified with metallocene, preferably during synthesis. The catalyst system is used to polymerise α-olefins, such as propylene.

DESCRIPTION OF THE PRIOR ART: Polyolefin manufacturing processes typically involve the polymerization of olefin monomer with an organometallic catalyst of the Ziegler-Natta type. Catalyst systems for the polymerization of olefins are well known in the art. Typically, these systems include a Ziegler-Natta type polymerization catalyst component; a co-catalyst, usually an organoaluminum compound; and an external electron donor compound or selectivity control agent, usually an organosilicon compound. Examples of such catalyst systems are shown in the following U.S. Patents: 4,107,413; 4,294,721; 4,439,540; 4,115,319; 4,220,554; 4,460,701; and 4,562,173; the disclosures of these patents are hereby incorporated by reference.

A Ziegler-Natta type polymerization catalyst is basically a complex derived from a halide of a transition metal, for example, titanium, chromium or vanadium with a metal hydride and/or a metal alkyl, typically an organoaluminum compound, as a co-catalyst. The catalyst is usually comprised of a titanium halide supported on a magnesium compound complexed with an alkylaluminum co-catalyst.

It is known that two or more homogeneous catalysts, such as those based on metallocene compounds, may be combined to effect properties, such as molecular weight distribution. U.S. Patent No. 4,530,914 discloses use of a catalyst system comprising two or more metallocenes in the polymerization of α-olefins, primarily ethylene, to obtain a broad molecular weight distribution. The metallocenes each have different propagation and termination rate constants. The metallocenes are mixed with an alumoxane to form the catalyst system.

It is also known that metallocenes may be affixed to a support to simulate a heterogeneous catalyst. U.S. Patent No. 4,808,561 discloses reacting a metallocene with an alumoxane and forming a reaction product in the presence of a support. The support is a porous material like talc, inorganic oxides such as Group IIA, IIIA IVA or IVB metal oxides like silica, alumina, silica-alumina, magnesia, titania, zirconia and mixtures thereof, and resinous material such as polyolefins, e.g., finely divided polyethylene. The metallocenes and alumoxanes are deposited on the dehydrated support material.

In U.S. Patent No. 4,701,432 a support is treated with at least one metallocene and at least one non-metallocene transition metal compound. To form a catalyst system a cocatalyst comprising an alumoxane and an organometallic compound of Group IA, IIA, IIB and IIIA is added to the supported metallocene/non-metallocene. The support is a porous solid such as talc or inorganic oxides or resinous materials, preferably an inorganic oxide, such as silica, alumina, silica-alumina, magnesia, titania or zirconia, in finely divided form. By depositing the soluble metallocene on the support material it is converted to a heterogeneous supported catalyst. The transition metal compound, such as $TiCl_4$, is contacted with the support material prior to, after, simultaneously with or separately from contacting the metallocene with the support.

It is known that Cp_2TiCl_2 in the presence of alkylaluminum compounds polymerizes ethylene but not propylene whereas in the presence of methylalumoxane (MAO) Cp_2TiCl_2 polymerizes propylene also to produce atactic polypropylene. Combination of dimethyl titanocene and its Cp-substituted analogues and $TiCl_3$ for propylene polymerizations has been reported in U.S. Patent No. 2,992,212 and in "Thermoplastic Elastomers Based on Block Copolymers of Ethylene and Propylene", G. A. Lock, Advances in Polyolefins, p. 59-74, Raymond B. Seymour, Ed. MAO was not used in this polymerization.

It would be advantageous to change polymer properties in a polymerization processes by using a supported Ziegler-Natta catalyst which has been modified by metallocene compound.

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to change polymer properties in polymerization processes using a supported Ziegler-Natta catalyst which has been modified with a metallocene compound.

Also, an object of this invention is to produce a polyolefin having high molecular weight and broad molecular weight distribution.

These and other objects are accomplished by a catalyst system comprising a supported Ziegler-Natta catalyst modified with a metallocene compound as an additive used in a polymerization process for polymerizing olefins, especially propylene.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides for a catalyst for polymerization of olefins comprising:

a) a supported Ziegler-Natta transition metal catalyst component modified with a metallocene compound as an additive in the synthesis of the catalyst component;

c) an aluminum trialkyl co-catalyst; and

d) an external electron donor.

The present invention also provides a process for the polymerization of olefins using the catalyst system described above comprising:

a) selecting a conventional Ziegler-Natta transition metal catalyst component modified with a metallocene compound;

b) contacting the catalyst component with an organoaluminum co-catalyst compound;

c) contacting the catalyst component with an electron donor either after or simultaneously with step b) to form a catalyst system;

d) introducing the catalyst system into a polymerization reaction zone containing a monomer under polymerization reaction conditions to form a polymer product; and

e) extracting polymer product from the polymerization reaction zone.

The polymer product extracted from the reactor has a broad molecular weight distribution.

A Ziegler-Natta catalyst may be pre-polymerized to improve the performance of the catalyst. Generally, a prepolymerization process is effected by contacting a small amount of monomer with the catalyst after the catalyst has been contacted with the electron donor. A pre-polymerization process is described in U.S. Patent Nos. 4,767,735, 4,927,797 and 5,122,583, hereby incorporated by reference.

Any of the conventional supported Ziegler-Natta transition metal compound catalyst components can be used in the present invention. The transition metal compound is preferably of the general formula MR^1_x where M is the metal, R^1 is a halogen or a hydrocarbyloxy and x is the valence of the metal. Preferably, M is a Group IVB metal, more preferably a Group IVB, and most preferably titanium. Preferably, R^1 is chlorine, bromine, an alkoxy or a phenoxy, more preferably chlorine or ethoxy and most preferably, chlorine. Illustrative examples of the transition metal compounds are $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $TiO(C_6H_{13})_2Cl_2$, $Ti(OC_2H_5)_2Br_2$ and $Ti(OC_{12}H_{25})Cl_3$. Mixtures of the transition metal compounds may be used. No restriction on the number of transition metal compounds is made as long as at least one transition metal compound is present.

The support should be an inert solid which is chemically unreactive with any of the components of the conventional Ziegler-Natta Catalyst. The support is preferably a magnesium compound. Examples of the magnesium compounds which are to be used to provide a support source for the catalyst component are magnesium halides, dialkoxymagnesiums, alkoxymagnesium halides, magnesium oxyhalides, dialkylmagnesiums, magnesium oxide, magnesium hydroxide, and carboxylates of magnesium.

The organoaluminum co-catalyst is preferably an aluminum alkyl of the formula $AlR^\wedge_3$ where $R^\wedge$ is an alkyl having 1-8 carbon atoms, R' being the same or different. Examples of aluminum alkyls are trimethyl aluminum (TMA), triethyl aluminum (TEAl) and triisobutyl aluminum (TiBAl). The preferred aluminum alkyl is TEAl.

The term "electron donor" as used herein, refers to the external electron donor or selectivity control agent (SCA). The external electron donor acts as a stereoregulator to control the amount of atactic form of polymer produced. It may also increase the production of isotactic polymers. The electron donor for the present invention is any one of the stereoselectivity control agents which are effective with Ziegler-Natta catalysts. Typically, an electron donor is an organosilicon compound. The electron donors included in the present invention are organic silicon compounds such as those described by the following formula:

$$SiR_m(OR^\#)_{4-m}$$

where R is an alkyl group, a cycloalkyl group, an aryl group or a vinyl group, $R^\#$ is an alkyl group, m is 0-4, R may be the same or different, $R^\#$ may be the same or different. Examples of electron donors are cyclohexylmethyldimethyoxysilane (CMDS), diphenyldimethoxysilane (DPMS) and isobutyl trimethoxysilane (IBMS). Over examples of electron donors are disclosed in U.S. Patent Nos. 4,218,339; 4,395,360; 4,328,122; 4,473,660; 4,562,173 and 4,547,552, which are hereby incorporated by reference. The preferred electron donor is CMDS.

The metallocene compound may be a cyclopentadienide, i.e., a metal derivative of a cyclopentadiene. The metallocene should contain at least one cyclopentadiene ring and be of the general formula:

$$R''_n(CpR_{5-n})_a(CpR'_{5-n})_{yb}M'R^*_{v-(a+b)}$$

where Cp is a cyclopentadienyl ring, R and R' are substituents on the cyclopentadienyl rings and can be a hydride or a hydrocarbyl from 1-9 carbon atoms, each R and R' being the same or different, each (CpR_{5-n}) and (CpR'_{5-n}) being the

same or different, a and b are 0 or 1, indicating whether the particular Cp ring is present, but at least one of a or b must be 1; R" is a structural bridge between $(CpR_{5-n})_a$ and $(CpR'_{5-n})_b$ to impart stereorigidity, n being 1 or 0 to indicate whether the bridge is present or not and when n=1, a and b both must equal 1; M' is Group IVB metal, R^* is a hydride, a halogen or a hydrocarbyl from 1-20 carbon atoms, v is the valence of M'. Preferably, a is 1 and b is 1, (CpR_{5-n}) and (CpR'_{5-n}) are the same and are cyclopentadienyl rings such that they are unsubstituted cyclopentadienyl and n is 0, i.e., unbridged. Preferably, M' is titanium, which have valences of 4. Preferably, R^* is a halogen or alkyl, most preferably chlorine or methyl.

The standard synthesis procedure is:

a) selecting a solid component comprising magnesium dialkoxide of the general formula $Mg(OR^2)_2$ where R^2 is a hydrocarbyl or substituted hydrocarbyl of 1 to 20 carbon atoms;
b) adding a chlorinating agent; and
c) adding a titanating agent.

The synthesis procedure for Ziegler-Natta type catalysts for the polymerization of olefins is disclosed in U.S. Patent Nos. 3,574,138; 3,642,746; 4,069,169; 4,226,741; 4,636,486; 4,816,433; 4,839,321 and 4,927,797, the disclosures of which are hereby incorporated. The present invention modifies the synthesis procedure, and thus modifies the catalyst, by adding a metallocene compound during the synthesis process. The specific synthesis procedure used was:

a) selecting a solid component comprising magnesium diethoxide;
b) adding titanium tetrachloride;
c) heating to promote reaction;
d) washing with heptane;
e) adding titanium tetrachloride;
f) heating to promote reaction;
g) drying in a vacuum.

The metallocene compound was added :

1) prior to the first addition of titanium tetrachloride,
2) during heating following the first addition of titanium tetrachloride,
3) prior to the second addition of the titanium tetrachloride or
4) during heating following the second addition of titanium tetrachloride.

The amount of metallocene added is such that a molar ratio of titanium tetrachloride added in either steps b) or e) to metallocene (Ti/Cp) is at least 5, preferably about 5 to about 200, more preferably about 20 to about 100 and most preferably is about 100.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

PREPARATION OF THE CATALYST

COMPARATIVE EXAMPLE

A round-bottom flask having a capacity of 500 ml and provided with a stirrer, the inner atmosphere of which was sufficiently substituted with nitrogen gas, was charged at room temperature with 10 g of diethoxy magnesium and 80 ml of toluene to form a slurry. The slurry was heated to 90°C on an oil bath. Next, 20 ml of $TiCl_4$ were added dropwise to the slurry while stirring. Then, 2.7 ml of n-butyl phthalate were added and the temperature was further elevated to 115°C and maintained for two hours with stirring. After cooling to 90°C, stirring ceased and precipitate was allowed to settle. The solid was separated and washed twice with 200 ml of toluene. While maintaining the temperature at 90°C, the solid was slurried in 80 ml of toluene. 20 ml of $TiCl_4$ were added dropwise to the composition and the resulting mixture was heated with stirring to a temperature of 115°C which was maintained for 2 hours. After the reaction, the composition was cooled to 90 °C, stirring ceased and the solid allowed to settle. The solid was separated, the temperature decreased to 40°C and was washed five times with 150 ml of n-heptane. The resulting catalyst component was dried in vacuum with heat to 35-40°C to yield a dry powder.

EXAMPLE 1

The catalyst was synthesized using the procedure of the Comparative Example except after the addition of diethoxy magnesium and toluene and before adding $TiCl_4$, 9.2 mmoles of Cp_2TiCl_2 was added as a slurry in toluene at room temperature.

EXAMPLE 2

The catalyst was synthesized using the procedure of Example 1 except that 1.8 moles of Cp_2TiCl_2 was used.

EXAMPLE 3

The catalyst was synthesized using the procedure of the Comparative Example except after the addition of diethoxy magnesium, toluene, $TiCl_4$ and n-butyl phthalate, 18.5 mmoles of Cp_2TiCl_2 was added after one hour of heating at 115°C.

EXAMPLE 4

The catalyst was synthesized using the procedure of Example 3 except that 9.2 mmoles of Cp_2TiCl_2 was used.

EXAMPLE 5

The catalyst was synthesized using the procedure of Example 3 except that 1.8 mmoles of Cp_2TiCl_2 was used.

EXAMPLE 6

The catalyst was synthesized using the procedure of the Comparative Example except prior to the second addition of $TiCl_4$; 4.6 mmoles of Cp_2TiCl_2 was added at 90°C with stirring for fifteen minutes.

EXAMPLE 7

The catalyst was synthesized using the procedure of Example 6 except that 1.8 mmoles of Cp_2TiCl_2 was used.

EXAMPLE 8

The catalyst was synthesized using the procedure of Example 6 except that 0.9 mmoles of Cp_2TiCl_2 was used.

EXAMPLE 9

The catalyst was synthesized using the procedure of Example 6 except that 0.45 mmoles of Cp_2TiCl_2 was used.

EXAMPLE 10

The catalyst was synthesized using the procedure of the Comparative Example except after the second addition of $TiCl_4$ and heating at 115°C with stirring for 1 hour, 1.8 mmoles of Cp_2TiCl_2 was added and the heating and stirring continued for another hour.

SUMMARY OF POLYMERIZATION CONDITIONS

wt. of catalyst:	10.0 mgrams
amount of TEAl (co-catalyst):	1.0 mmoles
Al/Ti ratio	200*
amount of CMDS (donor):	0.02 and 0.10 mmoles
Al/Si ratio	50 and 10, respectively
Hydrogen	16 mmoles
Propylene:	720g (1.4L)
Temp.:	70°C
Time:	60 mins.

* excluding titanium from metallocene

Prior to a polymerization run, all traces of moisture and air were expelled from a 2 L reactor by heating to a temperature over 100°C for a minimum of 30 minutes under a constant purge of dry nitrogen. Following this heating, the reactor was cooled to room temperature (25°C) under nitrogen. The reactor was stabilized at room temperature and then the hydrogen and 1.0 L of propylene were added. The reactor was then stirred at 1000 rpm. The TEAl co-catalyst and the CMDS electron donor were added to a 40 cc tubular reaction vessel. A catalyst as prepared in the Examples above was slurried in mineral oil suspension and added to the 40 cc reaction vessel. The co-catalyst/electron donor mixture was allowed to precontact approximately five minutes, and the final mixture with catalyst was allowed to contact for approximately two minutes prior to use. The 40 cc reaction vessel was then attached to an entry point on the 2 L reactor and the catalyst mixture was flushed into the 2 L reactor with room temperature liquid propylene. The reactor temperature was then raised to 70°C. The total amount of propylene present in the reactor was about 1.4 L. The polymerization reaction was allowed to proceed for one hour, at which point it was terminated by venting the excess propylene and cooling the reactor to room temperature. The reactor was then opened to collect the polymer product which was dried and analyzed. The molecular weight distribution or polydispersity (D) given as the ratio of weight-average to number-average molecular weight (Mw/Mn) was determined by gel permeation chromatography (GPC). The polymerization results are tabulated in Table 1.

TABLE 1

Example	Ti/Cp	D (Mw/Mn)
Comparative	0	6.48
1	10	11.0*
2	50	8.54
3	5	9.62
4	10	14.4*
5	50	10.71
6	20	14.96
7	50	13.9*
8	100	18.8*
9	200	14.78
10	50	10.38

*Average results of more than one run at the same conditions

The data above indicates that addition of a metallocene in the synthesis of a catalyst broadens the polydispersity of polypropylene. Preferably, the metallocene is added prior to the second addition of titanium tetrachloride.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Claims

1. A process for the polymerization of olefins using the catalyst system comprising:

   a) providing a Ziegler-Natta catalyst component containing a metallocene of the general formula:

   $$R''_n(CpR_{5-n})_a(CpR'_{5-n})_bM'R^*_{v-(a+b)}$$

   where Cp is a cyclopentadienyl ring, R and R' are substituents on the cyclopentadienyl rings and can be a hydride or a hydrocarbyl from 1-9 carbon atoms, each R and R' being the same or different, each (CpR_{5-n}) and (CpR'_{5-n}) being the same or different, a and b are 0 or 1, indicating whether the particular Cp ring is present, but at least one of a or b must be 1; R" is a structural bridge between $(CpR_{5-n})_a$ and $(CpR'_{5-n})_b$ to impart stereorigidity, n being 1 or 0 to indicate whether the bridge is present or not; M' is Group IVB metal, R^* is a hydride, a halogen or a hydrocarbyl from 1-20 carbon atoms, v is the valence of M',

   as an additive;

   b) contacting the catalyst component with an organoaluminum co-catalyst compound to form an active catalyst wherein the co-catalyst is described by the formula AlR'_3 where R' is an alkyl of from 1-8 carbon atoms and R' may be the same or different;
   c) introducing the catalyst into a polymerization reaction zone containing an olefin monomer under polymerization reaction conditions to form a polymer product;
   d) extracting the polymer product from the reactor.

2. A process for the polymerization of propylene using the catalyst system comprising:

   a) providing a Ziegler-Natta catalyst component containing a metallocene of the general formula:

   $$R'_n(CpR_{5-n})_a(CpR'_{5-n})_bM'R^*_{v-(a+b)}$$

   where Cp is a cyclopentadienyl ring, R and R' are substituents on the cyclopentadienyl rings and can be a hydride or a hydrocarbyl from 1-9 carbon atoms, each R and R' being the same or different, each (CpR_{5-n}) and (CpR'_{5-n}) being the same or different, a and b are 0 or 1, indicating whether the particular Cp ring is present, but at least one of a or b must be 1; R" is a structural bridge between $(CpR_{5-n})_a$ and $(CpR'_{5-n})_b$ to impart stereorigidity, n being 1 or 0 to indicate whether the bridge is present or not; M' is Group IVB metal, R^* is a hydride, a halogen or a hydrocarbyl from 1-20 carbon atoms, v is the valence of M',

   as an additive;

   b) contacting the catalyst component with an organoaluminum co-catalyst compound to form an active catalyst wherein the co-catalyst is described by the formula AlR'_3 where R' is an alkyl of from 1-8 carbon atoms and R' may be the same or different;
   c) introducing the catalyst into a polymerization reaction zone containing propylene under polymerization reaction conditions to form polypropylene;
   d) extracting polypropylene from the reactor having a molecular weight distribution of greater than or equal to 12.0.

3. A process for the polymerization of propylene as recited in Claim 2 wherein (CpR_{5-n}) and (CpR'_{5-n}) are the same and are unsubstituted cyclopentadienyl.

4. A process for the polymerization of propylene as recited in Claim 2 wherein the metallocene compound is bis(cyclopentadienyl) titanium dichloride.

5. A process for the polymerization of propylene as recited in Claim 2 wherein the co-catalyst is an aluminum alkyl of the formula $AlR^{\wedge}_3$ where R^ is an alkyl having 1-8 carbon atoms, R' being the same or different.

6. A process for the polymerization of propylene as recited in Claim 5 wherein the co-catalyst is trimethyl aluminum, triethyl aluminum or triisobutyl aluminum.

7. A process for the polymerization of propylene as recited in Claim 6 wherein the co-catalyst is triethyl aluminum.

8. A process for making a catalyst component comprising:

1) selecting a solid component comprising magnesium alkoxide;
2) adding a chlorinating agent;
5) adding a titanating agent;

wherein a metallocene of the general formula:

$$R"_n(CpR_{5-n})_a(CpR'_{5-n})_bM'R^{*}_{v-(a+b)}$$

where Cp is a cyclopentadienyl ring, R and R' are substituents on the cyclopentadienyl rings and can be a hydride or a hydrocarbyl from 1-9 carbon atoms, each R and R' being the same or different, each (CpR_{5-n}) and (CpR'_{5-n}) being the same or different, a and b are 0 or 1, indicating whether the particular Cp ring is present, but at least one of a or b must be 1; R" is a structural bridge between $(CpR_{5-n})_a$ and $(CpR'_{5-n})_b$ to impart stereorigidity, n being 1 or 0 to indicate whether the bridge is present or not; M' is Group IVB metal, R^{*} is a hydride, a halogen or a hydrocarbyl from 1-20 carbon atoms, v is the valence of M
is added prior to step 2), during step 3), prior to step 5) or during step 6).

9. The process for making a catalyst as recited in Claim 8 wherein the metallocene is added prior to step 5).

10. A process for making a catalyst as recited in Claim 8 wherein (CpR_{5-n}) and (CpR'_{5-n}) are the same and are unsubstituted cyclopentadienyl.

11. A process for the polymerization of propylene as recited in Claim 8 wherein the metallocene compound is bis(cyclopentadienyl) titanium dichloride.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 9105

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	EP-A-0 412 750 (MITSUBISHI) * example 2 * * claim 11 *	1,3,4 2,5-7	C08F10/00
X A	EP-A-0 436 328 (MITSUI) * examples 1,10,13 * * claim 1 *	1,3,4 2,5-7	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	1 October 1996	Fischer, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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